LARGE SCALE REDUCTIVE CLEAVAGE OF DIBENZOTHIOPHENE

John C. DiCesare* and Bryan M. White
Department of Chemistry and Biochemistry, The University of Tulsa, Tulsa, Oklahoma 74104

Abstract: A modified procedure for the large scale reductive cleavage of dibenzothiophene to prepare 2-phenylthiophenol without the formation of the over reduction products, hydrogen sulfide and biphenyl, has been developed.

2-Phenylthiophenol is an important intermediate in the hydrodesulfurization of dibenzothiophene, a common component of crude oil (1). Knowledge of the precise thermochemical properties of 2-phenylthiophenol is needed to develop improvements in refinery design and other petroleum processing technology. A large, high purity (>99.9%) sample of 2-phenylthiophenol was needed for thermodynamic studies (2). 2-Phenylthiophenol can be synthesized directly from dibenzothiophene by reductive cleavage using lithium or lithium biphenyl as the reducing agent followed by addition of aqueous acid to quench the resulting dianion. The yields of these reactions were modest, 40 - 60%, for the purified product (1a, 3).

Our attempts to synthesize 2-phenylthiophenol by the lithium biphenyl method resulted in similar yields. The formation of hydrogen sulfide upon quenching with aqueous acidic solution was an indication of over reduction to form biphenyl. Hydrogen sulfide is an OSHA regulated chemical with exposure limits in the 10-50 ppm range (4). A procedure that eliminated the formation of hydrogen sulfide would be beneficial, especially for larger scale preparations. The formation of biphenyl and hydrogen sulfide could occur either in the initial addition of reagents or as a competitive process during the course of the reaction. In order to elucidate when the formation was occurring, lithium naphthalide was utilized as the reducing agent (5).

The change in reducing agent was needed to determine when biphenyl was being produced, since the end product of lithium biphenyl is the same as the over reduction product. The progress of the reaction was monitored by quenching aliquots with aqueous acid and analyzing the ratio of dibenzothiophene, naphthalene, 2-phenylthiophenol and biphenyl formed in the reaction. It was found that biphenyl was being formed early in the course of the reaction. The literature procedures call for adding dibenzothiophene to a 0 °C solution of reducing agent. This procedure allows for excess reducing agent to be present during the addition of the dibenzothiophene, a situation facilitating over reduction especially during large scale reactions where addition times are greatly increased. Attempts to reverse the addition of reagents by adding the reducing agent to the cooled solution of dibenzothiophene by cannula resulted in some initial formation of the biphenyl dianion presumably from localized high concentration gradients of lithium naphthalide.

It was discovered that cooling the reaction below -20 °C effectively stopped all reactions from taking place. Therefore, cooling a solution of lithium naphthalide to below -20 °C and maintaining the temperature while adding the dibenzothiophene via an addition funnel afforded a large scale preparation of 2-phenylthiophenol without the formation of biphenyl or hydrogen sulfide. After complete addition of dibenzothiophene, GC analysis showed that only starting material was present in the solution. The solution was allowed to warm to 0 °C and stirred until the reaction was complete. The solution was diluted with ethyl acetate and extracted with 1N NaOH, the aqueous solution was neutralized with 3N HCl and extracted with ethyl acetate. The final product was recrystallized from 2-propanol. Isolated and purified yields as high as 92% on the one mole scale have been achieved.

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